

TECHNOLOGICAL DEVELOPMENT IN THE COAL AND HEAVY PETROLEUM UP-GRADING TO FUTURE SOCIETY

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INTRODUCTION

Energy basically obtained from the fossil carbonaceous resources on the earth will suffer the shortage of supply principally due to rapidly growing demand in the developing countries of large population. Huge consumption of the resources will bring about significant damages to the global environment. Hence, extensive up-grading of petroleum and coal at very high efficiency, energy saving, and environmental protection should be pursued at the same time. The correct structure of fossil resources, molecular transformation of their complete conversion and reforming by multi-stage scheme, catalysis and catalyst designs for the respective stage, molecular transformation into the carbon of high performances for energy saving and environmental protection are the targets of current research.

In the present paper, concepts and results in such areas that have been studied by the author for 20 years are overviewed.

Structural Understanding of Coal and Petroleum

Coal and petroleum are both complex mixtures of hydrocarbons. Their heaviest ends are targets of detail structural analyses.

Coal has been characterized by its maceral compositions and ranks, which tell us empirical but useful correlations on its properties. Recent approach is to clarify its structure on molecular basis. Basically heavy molecules in the coal are polynuclear polyaromatic hydrocarbons with heteroatoms and alkyl substituents. Sizes of molecule and aromatic ring, number of nuclei, bindings among nuclei, moiety of heteroatoms, number and length of alkyl substituents are primary factors of molecules. The distribution of the factors is concerned while the molecular weight is estimated around 1500. Such macromolecular chains are entangled each other to form colloid or micelle which occludes smaller molecules. The bridges among the chains can be covalent or non-covalent. Recent study indicates that non-covalent bonds among the chains are breakable rather easily by physical as well as chemical pretreatment at least in active macerals, providing high solubility and fusibility after the liberation. Non-covalent bridges are hydrogen bond, charge transfer interaction, aromatic ring stacking and metallic ion bridges. The author emphasized the carboxyl linkage and their coordination to divalent cations in lower ranking coals as shown in Figure 1. Although the complete picture of coal molecules is not disclosed yet, analysis based on such a profile of molecules gives us an image of its chemical nature.

The asphaltene is another target of structural study, while the molecules in naphtha, gas oil, vacuum gas oil and maltene are fairly clarified, their accuracy depending on their molecular size and type of structure. The asphaltene is soluble in benzene, but is believed to be present in the micelle or an entangled assembly, molecular weight of the component being beyond 10,000. Molecular assembly of the asphaltene in vacuum residue should be clarified at elevated and ambient temperatures. The present authors have hydrogenated 99% of hexane insoluble component into hexane soluble. Interestingly, solubilized asphaltene inherits the basic metal porphyrin structures. Structural change at this solubilization gives us some keys to elucidate the molecular assembly in the asphaltene.

Molecular Transformation of Coal and Heavy Petroleum

When coal and heavy fraction of asphaltene are heated, their molecular assembly is to be liberated to give a fused state from coal and solution from the asphaltene. Solvent present or added plays an important role to produce such a liquid state. In another situation without adequate solvent or with strong intermolecular linkages, condensation reactions of macromolecules can take place within the cage of molecular assembly, giving less soluble and less fusible component. Hence, the decaugulation of molecular assembly prior to the heating is claimed by the author very favorable to suppress such retrogressive reactions. The condensed product, thus produced, is called char or isotropic carbon with least stacking of aromatic planes. The author emphasizes the importance of hydrogen donor and dissolving activity of the solvent.

The polymeric substances in the liquid state can be depolymerized through the breakage of the weakest intermolecular linkages. Such breakage can be spontaneous, hydrogenation assisted, and hydrogenolysis as schematically illustrated in Figure 2. The fissured linkage can be capped with hydrogen to give smaller molecules, otherwise another type of condensation reaction takes place to give large molecule of more stability, leading to carbonaceous product. Such a process can be defined as carbonization or coking, being a principle pathway to produce carbon materials of functionality or process-troubles such as sludge, plugging and carbonaceous poisons as described later. Competitive reaction scheme is illustrated in Figure 3. Hydrogenation-assisted and hydrogenolysis breakages are performed with hydrogen donors at rather high temperature and rapid heating.

The limitation in such mechanisms of depolymerization is certainly present in the reactivities of acceptors and donors, limiting the extent of depolymerization. The catalyst can

perform further depolymerization through the hydrogenation, acidic and hydro-cracking to give distillates.

Catalysis and Catalyst Design for the Molecular Conversion

The catalysts can hydrogenate the aromatic ring and break the single C-C, C-S, C-N, C-O bonds due to their hydrogenation activity originating from transition metal components and their acidity. The hydrogenation produces hydrogen donor, caps the free radical, and saturates the double bonds to be fissured by acidity. The aromatic ring can be opened into chain molecule through the successive steps of hydrogenation and acidic bond fission. Alkylation and trans-alkylation modify the nature of aromatic species.

The hydrogenation can suppress the retrogressive and coking reactions though the control of condensation reactions and enhancing fusibility or solubility. On the other hand, acidity of the catalyst adsorbs strongly the polar molecules, trapping them on the surface for a long time while the condensation reaction takes place consecutively, leading to the carbon or coke on the catalyst surface.

Demetallation, desulfurization, denitrogenation and deoxygenation are major catalytic reactions for up-grading the hydrocarbon fuels. The molecular conversions pathways involved in the reactions are now being schematically described, although the difficulty increases with increasing molecular size because of difficulty in their molecular identification.

Another important factor is the intermolecular interactions in the liquid phase and on the catalyst surface. In some combinations, such interaction enhances the reaction while retards the reaction in other cases. Desulfurization of gas oil has been described on molecular bases. Chemistry involved in the desulfurization of 4,6-dimethyldibenzothiophene has been clarified.

The catalysts of better performances such as longer life, easy recovery and regeneration as well as high activity and selectivity are continuously looked for. The catalytic species and support are combined to achieve high performance, their chemical as well as physical interactions being concerned. Carbon and titania are reported to provide non-polar surface of intimate interaction with the catalytic species. Very fine particles of carbon as photographed in **Figure 4** are well dispersed and recoverable from ash minerals. New materials and new combinations are examined to obtain multi-functions.

The catalysis schemes are designed to allow the best performances of the catalysts. Optimum conditions are present to the optimum feed on the respective catalyst. Multi-stage reaction scheme is thus appropriate for the complete and selective conversion of coal and heavy petroleum, selecting the best catalyst and conditions for the respective stage. Solvent plays an important role even in the catalytic reactions.

Molecular Conversion of Coal and Heavy Petroleum into Carbons of High Performances

Carbons produced from coal and heavy petroleum are very indispensable by their high performances in the modern industry. Blast furnace coke, needle coke, carbon fiber and a variety of carbon artifacts are the case. Majority of such carbons is graphitizable through the ordered stacking of aromatic planes which is built in the early stage of carbonization. The mesophase or discotic liquid crystal is the intermediate state and product, leading to such carbons.

It is emphasized that the condensation into large aromatic planes and their stacking are balanced by selecting the feed, additive, preparative conditions and even catalysts of easy separation to form the mesophase. The author particularly emphasized roles of additives of hydrogen donating and dissolving activity. Molecular structure and molecular assembly at micro-, meso- and macro-scopic levels have been analyzed, and their relation to their properties is established. **Figure 5** illustrates microscopic views of mesophase, its as-spun and carbonized fibers. Thus, the carbons of high performance are designed through the preparation of precursor, and control of carbonization, graphitization, and forming on chemical and physical bases.

Carbon Materials for Energy Saving and Environmental Protection

The energy saving and environmental protection are the key issues for the effective use of resources. Carbon can provide some of excellent devices for these purposes. High strength per weight, high thermal conductivity, rapid and large adsorption and desorption, catalytically active surface of carbon fiber and active carbon fibers are such cases. Detail structural control for aromatic molecules including substituents and heteroatoms, and their stacking is the base for the design of the mesophase pitch and hence its derived high performance carbons. Very high strength and thermal conductivity are now achieved from aromatic hydrocarbon derived mesophase pitches prepared with HF/BF₃.

The author proposed a novel scheme of SO_x and NO_x removal over activated carbon fibers of controlled surface as shown in **Figure 6**. The calcination after the activation was found very effective to increase the activity for SO_x oxidation and NO_x reduction.

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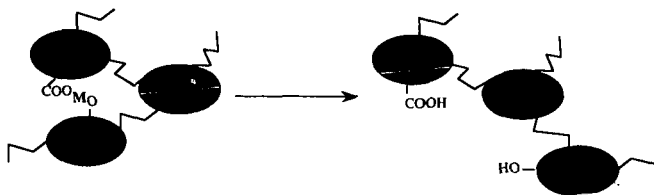


Figure 1 Coal Depolymerization Scheme through Decationing Treatment

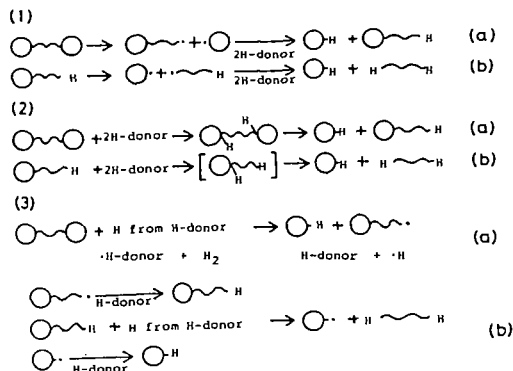


Fig.2 Hydrogen-transferring liquefaction mechanism
 (1) Hydrogenative stabilization of fragmental radicals
 (2) Hydrogenative bond-loosening
 (3) Hydrogenative bond-dissociation
 (molecular hydrogen participation)

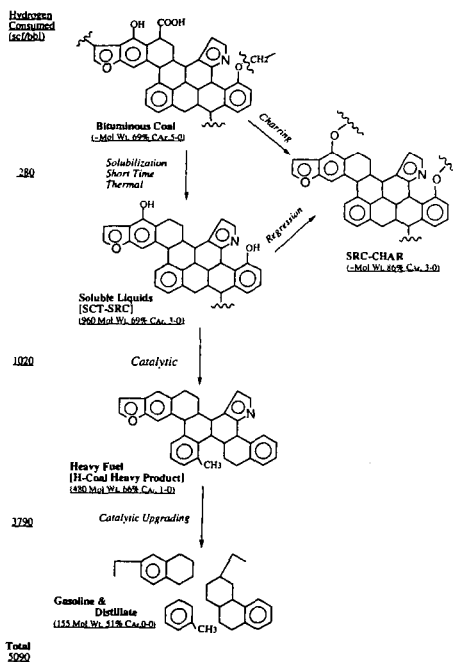


Figure 3 Structural Changes During Coal Liquefaction

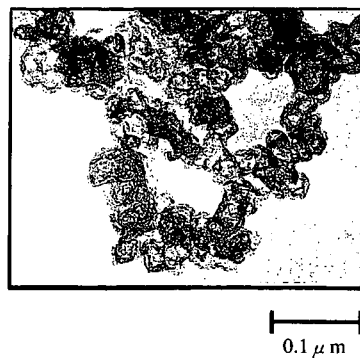


Figure 4 TEM photomicrograph of Ketjen Black

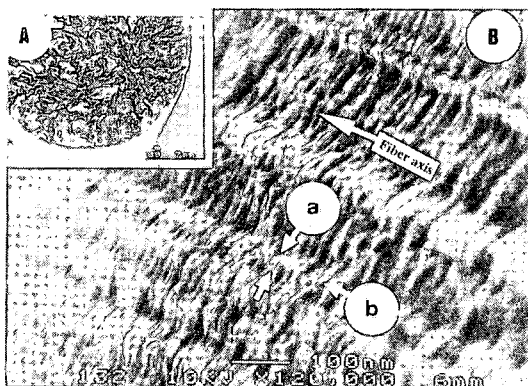


Figure 5 HR-SEM of mesophase pitch carbon fiber

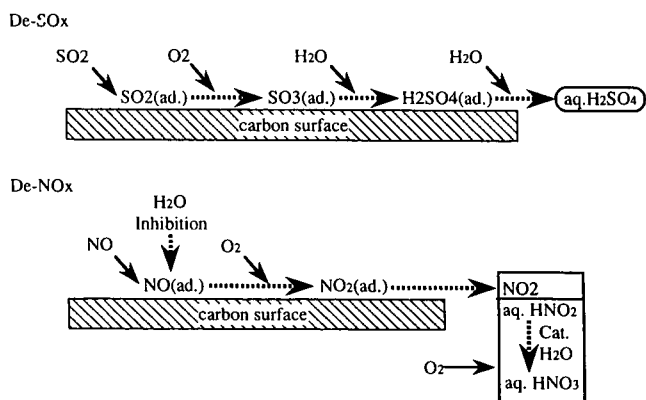


Figure 6 A Novel Scheme of SO_x and NO_x Removal over ACF